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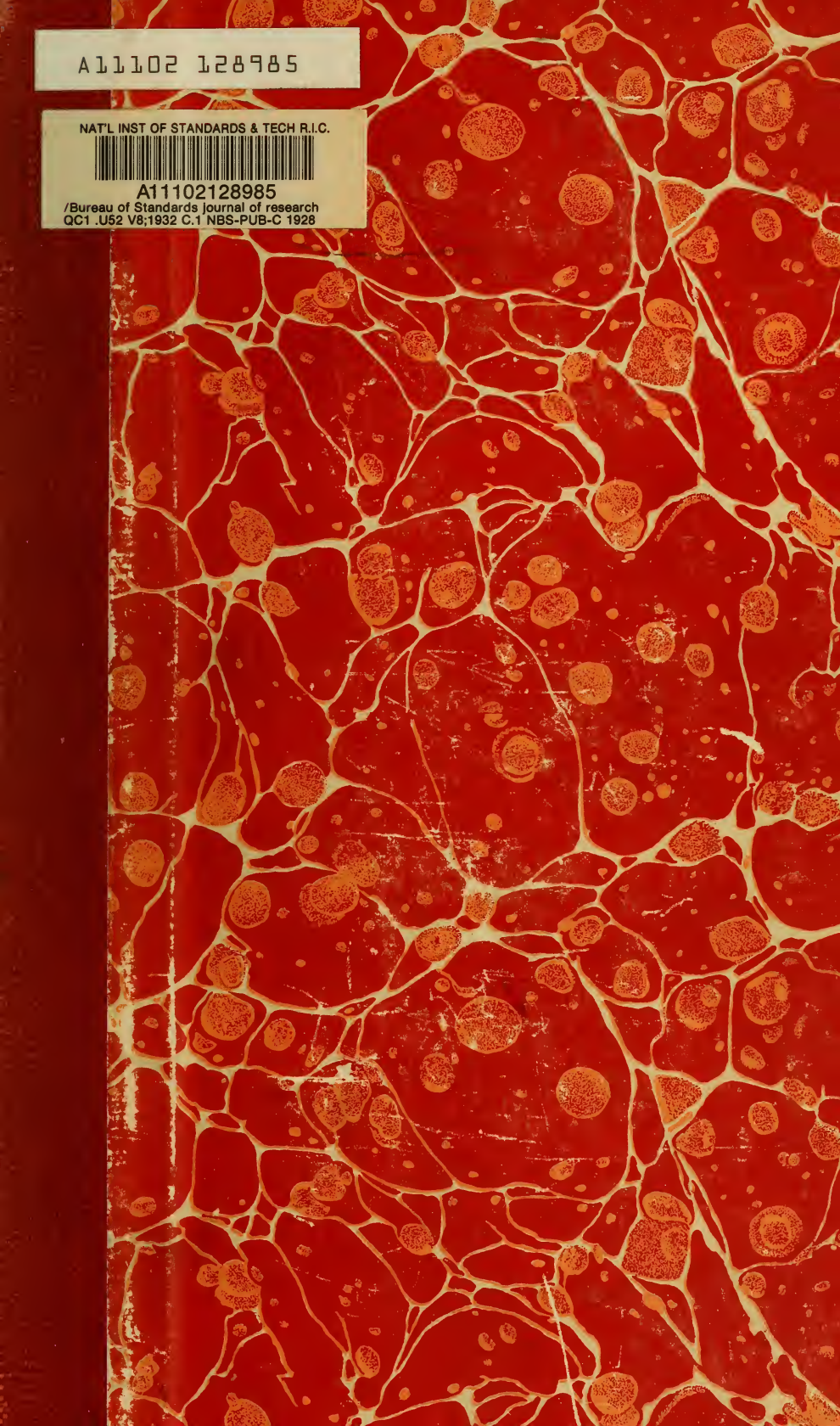

A METHOD FOR THE PURIFICATION OF RUBBER [1] AND PROPERTIES OF THE PURIFIED RUBBER

By A. T. McPherson

ABSTRACT

Purified rubber was prepared by the digestion of crude rubber or latex with water at about 190° C., followed by extraction with water and with alcohol, and drying in an atmosphere of inert gas. The digestion hydrolyzed the proteins, and the extraction removed the hydrolysis products, resins, and other impurities. The purified rubber contained about 99.5 per cent of rubber hydrocarbon. Properties of the rubber hydrocarbon at 25° C. were: Density, 0.9060; refractive index, 1.5184; dielectric constant at 1,000 cycles per second, 2.37; power factor at 1,000 cycles per second, 0.0015; conductivity at the end of 1 minute, 2.2×10^{-7} mho. The electrical properties measured on 14 samples were apparently independent of the botanical source or the kind of crude rubber.

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I. INTRODUCTION

This paper describes a simple procedure which was used to purify rubber for a study of the electrical properties of the system, rubber sulphur. The method of purification was one in which the non-hydrocarbon constituents of the raw rubber were removed by extraction, the proteins being first hydrolyzed by digestion with water at an elevated temperature. The solvents with which the rubber was extracted were water and alcohol. These removed the protein disintegration products, sugars, fatty acids, and other resinous and minor constituents, and yielded a product which was about 99.5

[1] The preparation of rubber hydrocarbon of high purity by the crystallization and distillation of rubber is the subject of a research being conducted by other investigators at this bureau. See Technical News Bulletin of the Bureau of Standards No. 161, p. 85; September, 1930. Also, E. W. Washburn, Crystalline Rubber Hydrocarbon, Phys. Rev., vol. 38, pp. 1790–91; 1931.

per cent rubber hydrocarbon. While this method of purification involves no distinctly original features it is here given in some detail, since it may be of interest to other investigators who may wish to prepare for experimental purposes large quantities of rubber hydrocarbon of reasonable purity without an excessive expenditure of time.[2]

The dielectric constant, power factor, and conductivity of purified rubber prepared from different kinds of crude rubber were relatively consistent, and showed no variations which might be attributed to the botanical source or kind of rubber.

II. DESCRIPTION OF THE PURIFICATION PROCESS

Various procedures were tried for the purification of rubber from latex or crude rubber. The procedure which proved the simplest and most generally satisfactory consisted in digestion with water, extraction with water and with alcohol, and drying in an inert gas.

1. DIGESTION WITH WATER

Crude rubber or latex was digested with water at an elevated temperature in an autoclave. The crude rubber, in lots of several kilograms, was sheeted thin and put into a Pyrex glass cylinder with sufficient water to cover it. The cylinder was placed in the autoclave in such a way that the rubber was not exposed to contamination by iron or copper salts from the autoclave or its fittings. Since the autoclave was heated by means of steam circulated through a jacket a quantity of water was placed in the bottom of the autoclave to facilitate heat transfer to the pyrex jar and its contents. Ammonia-preserved latex, when used instead of crude rubber, was placed in the pyrex cylinder with no previous treatment other than straining. The autoclave was heated to about 190° C., which is the temperature of steam at a pressure of 167 pounds per square inch in excess of atmospheric pressure. The time of digestion was ordinarily three to four hours, exclusive of the time required for heating and cooling the heavy autoclave. The time and temperature of heating were probably in excess of that necessary to hydrolyze the proteins, but were employed in order to insure thorough penetration of the crude rubber by the water.

At the conclusion of the digestion the water in which the rubber had been heated was dark colored and contained considerable organic matter. When latex was employed it was always found coagulated after digestion. A hand examination of the digested rubber indicated that the digestion process did not soften or degrade the rubber to any great extent.

2. WASHING WITH WATER AND ALCOHOL

The digested rubber was washed and extracted in order to remove protein disintegration products, resins, sugars, soluble inorganic salts, and possible mechanical impurities. The washing and extraction were carried out with the use of an internal mixer of a type which was designed for the compounding of rubber.[3] The mixing chamber

[2] This method is similar to the one described by Kemp, J. Franklin Inst., vol. 211, pp. 44–47; January, 1931. The work here reported was done prior to the publication by Kemp. See Technical News Bulletin of the Bureau of Standards, No. 128, pp. 2–3; December, 1927.

[3] This internal mixer is described in Technical News Bulletin of the Bureau of Standards, No. 141, pp. 1–2; January, 1929, and also in India Rubber World, vol. 80, No. 1, p. 78, April, 1929.

was provided with a cover fitted with a reflux condenser to prevent the loss of solvent. The mastication of the rubber with the solvent in the internal mixer was a much more effective means of removing these various impurities than was percolation of the thinly sheeted material with the solvent in an extraction apparatus. The chief advantage of the internal mixer lay in the constant renewal of the surface of the rubber. This facilitated the removal of any mechanical impurities and pockets of solution, and probably accelerated greatly the extraction of substances slightly soluble in rubber. Furthermore, the use of the internal mixer obviated various difficulties which are attendant on the extraction of soft rubber in lots of several kilograms in an apparatus of the Soxhlet type.

The process of washing and extracting the digested rubber with water usually occupied 4 hours, during which time the water was changed every 15 or 30 minutes. Distilled water was used, and was kept vigorously boiling in order to exclude air and thus prevent oxidation of the rubber. At the end of the period the wash water was practically colorless and left only a very slight residue on evaporation.

Treatment with water was followed by a similar treatment with alcohol. For this purpose ethanol, containing not over 5 per cent of water and 10 per cent of methanol, was used. Alcohol was employed as a solvent for extracting the resinous constituents of rubber rather than acetone on account of its higher boiling point. When rubber was extracted with acetone at its boiling point, 56° C., a soft and almost pasty product was obtained on account of the mechanical working of the rubber at the relatively low temperature.

Extraction with alcohol was followed by a few minutes extraction with one or two portions of boiling water in order to remove the alcohol. This was done because, in the subsequent drying, it seemed easier to remove the water than the alcohol. This point, however, was not investigated critically.

3. DRYING

The extracted rubber was dried by working it in the internal mixer at a temperature of 110° to 125° C. in an atmosphere of inert gas, usually nitrogen. A continuous stream of gas was passed through the mixer during the drying, which was ordinarily continued for about 30 minutes after steam had disappeared from the effluent gas.

III. COMPOSITION OF THE PURIFIED RUBBER

No extensive study was made of the composition of the purified rubber. Determinations of nitrogen, benzene-insoluble constituents, and ash were made on representative preparations. Combustion analyses of high precision were made on two samples of the purified rubber.

1. NITROGEN

Nitrogen was determined by the Kjeldahl method, using 2 g samples of rubber. The results of analyses on rubber before and after purification are given in Table 1. The nitrogen content of the original unpurified rubber was 0.3 to 0.6 per cent, while that of seven lots of the purified material ranged from 0.02 to 0.05 per cent, with an average value of about 0.03 per cent. The precision of the determination was of the order of 0.01 per cent.

2. ASH

Determinations of ash were made by igniting 5 g samples of rubber in crucibles of approximately 100 ml capacity in an electrically heated muffle furnace, observing the usual precautions. In most cases an appreciable reduction in ash content resulted from purification. Only in the case of a sample of Guayule rubber was there a small increase in percentage of ash. This may have resulted from the removal of a larger proportion of resins than of inorganic material in the purification process. The ash content of purified rubber made from clean plantation rubber or latex ranged from 0.04 to 0.24 per cent, with an average of about 0.12 per cent. Analyses made by ignition in a muffle and in a combustion furnace were in good agreement. Seven determinations on one preparation, by the former method, indicated an ash content of 0.15 ± 0.02 per cent, while five determinations by the latter method, which are reported in Table 2, gave the result 0.13 ± 0.03 per cent.

3. BENZENE-INSOLUBLE CONSTITUENTS

The benzene-insoluble fraction of rubber was determined by dissolving 5 g samples in 50 to 100 ml of benzene to which about 1 g of trichloroacetic acid had been added. On exposure to light for a few hours a limpid solution was obtained from which proteins, salts, and foreign materials, such as dirt or bark, could easily be separated by centrifuging. The residue was thoroughly washed with benzene and dried before it was weighed. The results which are given in Table 1 indicate that the original unpurified rubber contained from 2.5 to 5 per cent of insoluble material, and the purified rubber 0.1 to 0.3 per cent.

TABLE 1.—*Composition of rubber before and after purification*

Source of rubber	Preparation No.	Nitrogen		Benzene-insoluble		Ash	
		Before purification	After purification	Before purification	After purification	Before purification	After purification
		Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
Smoked sheet	3	0.29	0.02	2.50	0.18	0.18	0.08
Guayule [1]		.30	.05	8.1		1.03	1.27
Pale crêpe	6	.31	.02			.16	.14
	7		.03				
	8		.03				
	10		.02				.07
Latex-sprayed rubber	4	.62	.02	5.35	.26	1.4	.24
Hevea latex	11		.02				.04
	14						.15
	[2] 19		.004		.33		.19
	[3] 23				.13		.08
	[3] 27				.31		

[1] The Guayule rubber was digested with 4 per cent potassium hydroxide solution instead of water to destroy woody matter.

[2] This sample of purified rubber was prepared by A. D. Cummings using the method of Cummings and Sebrell, Ind. Eng. Chem. vol. 21, p. 553, June 1929.

[3] These samples were prepared and analyzed by A. D. Cummings.

4. CARBON, HYDROGEN, AND OXYGEN

Organic combustion analyses on three preparations of purified rubber were made with an apparatus capable of giving results of relatively high accuracy.[4] The results are shown in Table 2. The sums of the carbon, hydrogen, and ash found in the different analyses ranged from 99.82 to 100.06 per cent, with an average value of 99.95 per cent. Assuming the nitrogen content to be 0.03 per cent, the oxygen indicated by difference is only 0.02 per cent. This is evidence that practically all the resins and other nonhydrocarbon constituents were removed by the extraction process, and that the rubber did not suffer appreciable oxidation in the process of purification.

The above data do not warrant an exact statement of the purity of the rubber. If it is assumed, however, that the chief impurities are inorganic substances, proteins, or their degradation products and moisture, the sum of these is probably not in excess of 0.5 per cent, or the hydrocarbon content of the rubber may be estimated at about 99.5 per cent.

TABLE 2.—*Combustion analyses on purified rubber*

Source of rubber	Analysis No.	Carbon	Hydrogen	Ash	Total
		Per cent	*Per cent*	*Per cent*	*Per cent*
Pale crêpe	1	87.87	11.76	0.19	99.82
	2	87.75	11.95	.25	99.95
Hevea latex	1	87.99	11.89	.18	100.06
	2	88.05	11.87	.10	100.02
	3	87.95	11.87	.10	99.92
	4	87.94	11.85	.15	99.94
	5	88.01	11.86	.10	99.96
Calculated for C_5H_8		88.15	11.85	----------	100.00

IV. PROPERTIES OF THE PURIFIED RUBBER

The purified rubber was dark in color, except when viewed in thin layers. The colored constituents were probably present in small amount and originated during the digestion with water at the high temperature.

No measurements were made of the consistency of the purified rubber. By hand examination it seemed to be comparable to or somewhat softer than crude rubber which had been thoroughly masticated or "broken down." The consistency was probably the result of the mechanical working accorded the rubber during the extraction and drying.

Determinations of the density and the refractive index were made on single samples of the purified rubber which had been prepared from latex. Dielectric constant, power factor, and conductivity measurements were made on all samples of the purified rubber.

[4] These analyses were made by H. J. Wing using the method described by Washburn, Bruun, and Hicks, B. S. Jour. Research, vol. 2 (RP45), p. 487, March, 1929.

1. DENSITY

The density of the purified rubber was determined at three temperatures with the use of a Pyrex glass pyknometer in which mercury was employed as the confining liquid.[5] The density at 0° C. was 0.9209; at 20°, 0.9088; and at 61.2°, 0.8845. These values, when plotted against the temperature, lie on a straight line within probable experimental error, as is indicated by Figure 1. The density at 25°, taken from the curve in this figure, is 0.9060. The coefficient of change in density with temperature is 0.000595 per degree, between 0° and 61.2°, or the density at any temperature, t, in this range is given by the relation,

$$d_t = 0.9060 + 0.000595\ (25 - t)$$

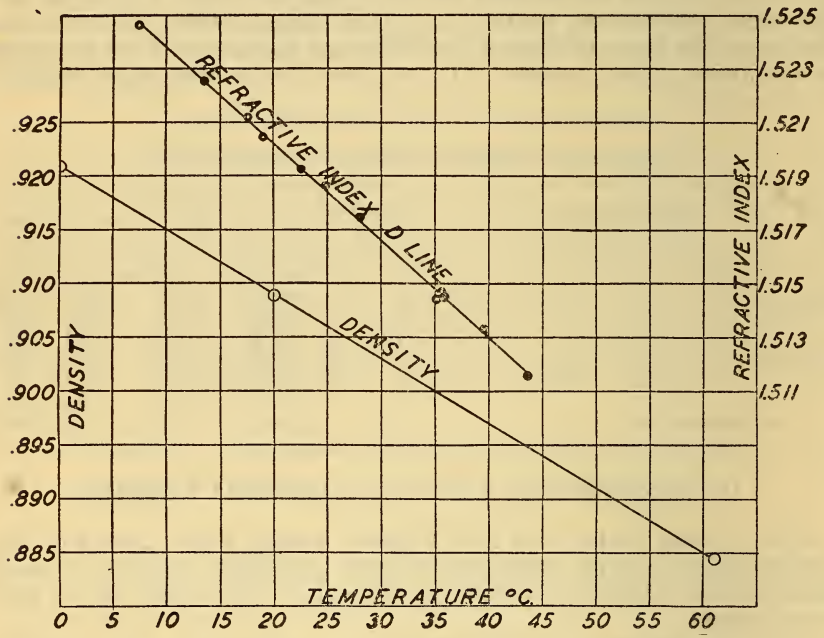

FIGURE 1.—*Density and refractive index of purified rubber*

By way of comparison the density of standard grades of commercial crude rubber at 25° C. is about 0.912, and the change in density per °C. is 0.00062.[6]

2. REFRACTIVE INDEX

The refractive index of the purified rubber for the D line of sodium was measured with an Abbé prism refractometer. Thin specimens suitable for measurement in this instrument were prepared by pressing out small sheets of rubber between layers of aluminum foil. These were applied to the prism and pressed against it so as to make optical contact without the use of a liquid. The temperature at which the determinations were made was controlled by circulating water around

[5] The density determinations were made by A. D. Cummings.
[6] A. T. McPherson, Density of Rubber-Sulphur Compounds, B. S. Sci. Paper, No. 560, 1927.

the prisms. The results which were obtained at temperatures from 7° to 43° C. are shown graphically in Figure 1.

The refractive index of the purified rubber for the *D* line at 25° C., taken from the curve in Figure 1, is 1.5184, which is approximately the same as the value 1.519 reported previously for crude rubber.[7] The refractive index at temperatures other than 25° C. is given by the relation

$$n^t_D = 1.5184 + 0.00036\ (25 - t)$$

The experimental results agree with the values indicated by this equation with a maximum deviation of 0.0004 and an average deviation of 0.0001.

3. ELECTRICAL PROPERTIES

Dielectric constant, power factor, and conductivity measurements were made on samples of purified rubber which had been prepared not only from wild and plantation Hevea rubber, but also from other natural rubbers of widely different botanical sources. The method of preparing test specimens and making electrical measurements is described fully elsewhere.[8] The results of these measurements are summarized in Table 3.[9]

The dielectric constant at 1,000 cycles per second and 25° C. of all the samples of purified rubber which were examined was between 2.33 and 2.40, with an average value of 2.37. The dielectric constant of the unpurified rubber is higher and more variable than this, ranging from 2.50 to 2.70 in most cases. The value, 2.37, probably approximates the dielectric constant of pure rubber hydrocarbon.

The power factor of purified rubber measured at 1,000 cycles per second was less than that of rubber before purification, and ranged from 0.0008 to 0.0026, with an average value of 0.0015. This variability, in the light of general knowledge of power factor, may be attributed to residual impurities in the rubber, including moisture. The true power factor of rubber hydrocarbon is probably less than 0.0008, the lowest value found, because traces of most impurities are known to increase the power factor of hydrocarbons above the true value.

The conductivity of purified rubber, measured one minute after the application of potential, was decidedly lower and less variable than that of crude rubber. For different samples the conductivity ranged from 1.4 to 3.6×10^{-17} mho, with an average of 2.2×10^{-17} mho. As in case of the power factor the average conductivity is not to be regarded as the true conductivity of a hydrocarbon, since the effect of impurities is always to increase, never to decrease, the conductivity of the main constituent. Consequently, the conductivity of pure rubber hydrocarbon is in all probability smaller than the lowest value here reported.

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[7] H. L. Curtis and A. T. McPherson, Dielectric Constant, Power Factor, and Resistivity of Rubber and Gutta-Percha, B. S. Tech. Paper No. 299, p. 698, 1925. See also Cecil W. Shacklock, Further Studies of Rubber Solutions, Inst. Rubber Ind., Trans. vol. 7, p. 356; 1932.

[8] H. L. Curtis, A. H. Scott, and A. T. McPherson, Properties of the System, Rubber Sulphur. Part III. Effect of Temperature and Frequency on the Dielectric Constant, Power Factor, and Conductivity. In preparation.

[9] The electrical measurements were made by A. H. Scott.

TABLE 3.—*Electrical properties of purified rubber at 25° C.*

Kind of crude rubber or latex	Botanical source	Preparation No.	Dielectric constant [1]	Power factor [1]	Conductivity [2]
					Mho×10^{17}
Penang	*Ficus elastica*		2.39	0.0018	2.7
Guayule [3]	*Parthenium argentatum*		2.33	.0011	3.7
Gaboon ball	Probably *Landolphia*		2.40	.0013	3.3
Fine Para	*Hevea brasiliensis*	2	2.37	.0008	1.6
Smoked sheet	do	3	2.36	.0008	1.6
Latex-sprayed	do	4	2.35	.0014	2.2
Pale crêpe	do	1	2.39	.0010	1.7
	do	6	2.36	.0017	1.5
	do	8	2.37	.0016	1.9
Ammonia-preserved latex	do	0	2.29	.0018	2.2
	do	11	2.36	.0018	2.0
	do	14	2.37	.0014	2.6
	do	27	2.39	.0026	
	do	31	2.41	.0022	1.7
Average for all samples			2.37	.0015	2.2

[1] The dielectric constant and power factor were measured at a frequency of 1,000 cycles per second.
[2] The conductivity was measured one minute after the application of potential.
[3] The purification of the guayule rubber used for these measurements included solution in benzene, filtration, and precipitation with acetone to effect the removal of woody impurities.

4. VULCANIZATION CHARACTERISTICS

No critical study was made of the vulcanization of purified rubber. Numerous samples, however, compounded with sulphur in proportions from 2 to 32 per cent by weight, exhibited a behavior on vulcanization that was apparently the same as that of similar mixtures of crude rubber and sulphur. When the samples were vulcanized from 20 to 40 hours at 140° C., the residual, uncombined sulphur was less than 0.1 per cent in all cases except those where the total sulphur was 28 to 32 per cent. In the latter cases residual sulphur was present in varying amounts up to 0.8 per cent.

WASHINGTON, April 16, 1932.